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I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation and Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General hereby certify that annexed hereto is a true copy of the international application filed on 24 June 2002 under the Patent Cooperation Treaty at the UK Receiving Office. The application was allocated the number PCT/GB2002/002846.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or the inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

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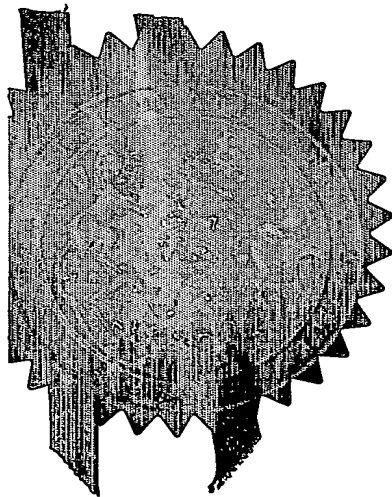
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Signed

HK Taylor

Dated

18 JUL 2003



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REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only	
PCT/GB 02 / 02 8 4 6	
International Application No.	
24 JUNE 2002	
International Filing Date 24.6.02	
United Kingdom Patent Office PCT International Application	
Name of receiving Office and "PCT International Application"	
Applicant's or agent's file reference (if desired) (12 characters maximum) UQI 51057/WO	

Box No. I TITLE OF INVENTION Cleaning Textiles	
Box No. II APPLICANT <input type="checkbox"/> This person is also inventor	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
Imperial Chemical Industries PLC 20 Manchester Square London W1U 3AN United Kingdom	Telephone No. 01642 432046 Facsimile No. 01642 436146 Teleprinter No. Applicant's registration No. with the Office
State (that is, country) of nationality: GB	State (that is, country) of residence: GB
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input checked="" type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
MOTSON, Harold Russell 10 Grantham Road Norton, Stockton-On-Tees, Cleveland, TS10 1PP United Kingdom	This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: GB	State (that is, country) of residence: GB
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
<input checked="" type="checkbox"/> Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: <input type="checkbox"/> agent <input type="checkbox"/> common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)	
ROBERTS, Jonathan Winstanley Uniqema Intellectual Property Department Wilton Centre Wilton, Redcar TS10 4RF United Kingdom	Telephone No. 01642 432046 Facsimile No. 01642 436146 Teleprinter No. Agent's registration No. with the Office
<input type="checkbox"/> Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

IRVINE, Derek John
24, Burnmoor Drive
Eaglescliffe, Stockton-on-Tees
TS16 0HZ
United Kingdom

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

APPELMAN, Eric
Adriaan Van Bleijenburgstraat 22
3311 LB Dordrecht
Netherlands

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:
NL

State (that is, country) of residence:
NL

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No. V DESIGNATION OF STATES

Mark the applicable check-boxes below; at least one must be marked.

The following designations are hereby made under Rule 4.9(a):

Regional Patent

- ☒ AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZM Zambia, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT (if other kind of protection or treatment desired, specify on dotted line)
- ☒ EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ EP European Patent: AT Austria, BE Belgium, CH & LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, TR Turkey, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GQ Equatorial Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | | |
|---|--|---|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> AG Antigua and Barbuda | <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> OM Oman |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> PH Philippines |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> IS Iceland | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> JP Japan | |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> BG Bulgaria | <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> KR Republic of Korea | <input checked="" type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> BZ Belize | <input checked="" type="checkbox"/> KZ Kazakhstan | <input checked="" type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> LC Saint Lucia | <input checked="" type="checkbox"/> SL Sierra Leone |
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| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> LR Liberia | <input checked="" type="checkbox"/> TM Turkmenistan |
| <input checked="" type="checkbox"/> CO Colombia | <input checked="" type="checkbox"/> LS Lesotho | <input checked="" type="checkbox"/> TN Tunisia |
| <input checked="" type="checkbox"/> CR Costa Rica | <input checked="" type="checkbox"/> LT Lithuania | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> LU Luxembourg | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
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| <input checked="" type="checkbox"/> DM Dominica | <input checked="" type="checkbox"/> MG Madagascar | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> DZ Algeria | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia | <input checked="" type="checkbox"/> US United States of America |
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| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> MW Malawi | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> MX Mexico | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> MZ Mozambique | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> NO Norway | <input checked="" type="checkbox"/> ZA South Africa |
| <input checked="" type="checkbox"/> GD Grenada | | <input checked="" type="checkbox"/> ZM Zambia |
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| <input checked="" type="checkbox"/> GH Ghana | | |

Check-boxes below reserved for designating States which have become party to the PCT after issuance of this sheet:

<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Supplemental Box

If the Supplemental Box is not used, this sheet should not be included in the request.

Continuation of Box IV

HUMPHRIES, Martyn
GRAHAM, John George

1. If, in any of the Boxes, except Boxes Nos. VIII(i) to (v) for which a special continuation box is provided, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No." (indicate the number of the Box) and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:
 - (i) if more than two persons are to be indicated as applicants and/or inventors and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
 - (ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
 - (iii) if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
 - (iv) if, in addition to the agent(s) indicated in Box No. IV, there are further agents: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;
 - (v) if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of addition," or if, in Box No. V, the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part": in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
 - (vi) if, in Box No. VI, there are more than five earlier applications whose priority is claimed: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI.
2. If, with regard to the precautionary designation statement contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1)				
item (2)				
item (3)				
item (4)				
item (5)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☐ all items
 ☐ item (1)
 ☐ item (2)
 ☐ item (3)
 ☐ item (4)
 ☐ item (5)
 ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)): . . .

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EP

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)

Number

Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

Number of
declarations

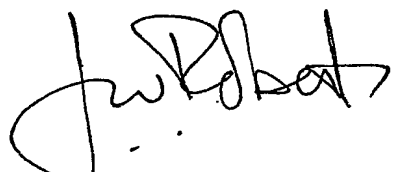
- | | | |
|---|--|---|
| <input type="checkbox"/> Box No. VIII (i) | Declaration as to the identity of the inventor | : |
| <input type="checkbox"/> Box No. VIII (ii) | Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent | : |
| <input type="checkbox"/> Box No. VIII (iii) | Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application | : |
| <input type="checkbox"/> Box No. VIII (iv) | Declaration of inventorship (only for the purposes of the designation of the United States of America) | : |
| <input type="checkbox"/> Box No. VIII (v) | Declaration as to non-prejudicial disclosures or exceptions to lack of novelty | : |

Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains:		This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):		Number of items
(a) the following number of sheets in paper form:		1. <input checked="" type="checkbox"/> fee calculation sheet	:	1
request (including declaration sheets) :	6	2. <input type="checkbox"/> original separate power of attorney	:	
description (excluding sequence listing part) :	7	3. <input type="checkbox"/> original general power of attorney	:	
claims :	3	4. <input type="checkbox"/> copy of general power of attorney; reference number, if any:	:	
abstract :	1	5. <input type="checkbox"/> statement explaining lack of signature	:	
drawings :	0	6. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s):	:	
Sub-total number of sheets :	17	7. <input type="checkbox"/> translation of international application into (language):	:	
sequence listing part of description (actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (b) below) :		8. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material	:	
Total number of sheets :	17	9. <input type="checkbox"/> sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CD-R or other))	:	
(b) sequence listing part of description filed in computer readable form		(i) <input type="checkbox"/> copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)	:	
(i) <input type="checkbox"/> only (under Section 801(a)(i))		(ii) <input type="checkbox"/> (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter	:	
(ii) <input type="checkbox"/> in addition to being filed in paper form (under Section 801(a)(ii))		(iii) <input type="checkbox"/> together with relevant statement as to the identity of the copy or copies with the sequence listing part mentioned in left column	:	
Type and number of carriers (diskette, CD-ROM, CD-R or other) on which the sequence listing part is contained (additional copies to be indicated under item 9(ii), in right column):		10. <input type="checkbox"/> other (specify):	:	
Figure of the drawings which should accompany the abstract:		Language of filing of the international application: English		

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).



ROBERTS, Jonathan Winstanley
Authorised Officer

For receiving Office use only		2. Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received:
1. Date of actual receipt of the purported international application:	24 JUNE 2002 24.6.02	
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid	

For International Bureau use only

Date of receipt of the record copy
by the International Bureau:

Cleaning Textiles

This invention relates to cleaning textile materials and products including clothes using liquid carbon dioxide (CO₂) and cleaning additives.

The dry cleaning of clothes using fluid carbon dioxide, either as liquid or supercritical fluid, is known from many patents. An early suggestion is in US 4012194 (Maffei) which teaches simply using liquid carbon dioxide as a substitute for halocarbon solvents e.g. perchlorethylene (perc), used in conventional dry cleaning. Later patents develop approaches using detergent materials, including US Patents US 5676705, US 5683473, US 5683977, US 6131421, US 6148644, and US 6299652 assigned to Unilever and their equivalents, which relate to the use of defined detergents based on various classes of polymers and a series of cases, including US Patents 5858022, 6200352, 6280481, 6297206, 6269507 and US published application 200106053 A, assigned to MiCell and their equivalents. Also US 5279615 assigned to Chlorox Co uses cleaning non-polar organic cleaning adjuncts, especially alkanes, in densified, particularly supercritical CO₂.

This invention is based on a liquid CO₂ dry cleaning medium including relatively polar multi-esters as cleaning additives which improve the cleaning performance of the liquid CO₂ and give improved handling characteristics as compared with the use of detergents available for use with liquid CO₂. The multi-esters are compounds having 2 or more carboxylic acid ester groups, and molecular weights of not more than 750.

The invention accordingly provides a detergent free dry cleaning medium based on liquid CO₂ and including from 0.01 to 5% by weight of the cleaning medium of a cleaning additive which is at least one multi-ester having a molecular weight of not more than 750.

Alternatively the invention provides a micelle free dry cleaning medium based on liquid CO₂ and including from 0.01 to 5% by weight of the cleaning medium of a cleaning additive which is at least one multi-ester having a molecular weight of not more than 750.

The invention includes a method of dry cleaning which includes contacting textile material, particularly clothes, with a detergent free dry cleaning medium based on liquid CO₂ and including from 0.01 to 5% by weight of the cleaning medium of a cleaning additive which is at least one multi-ester having a molecular weight of not more than 750.

Further alternatively, the invention includes a method of dry cleaning which includes contacting textile material, particularly clothes, with a micelle free dry cleaning medium based on liquid CO₂ and including from 0.01 to 5% by weight of the cleaning medium of a cleaning additive which is at least one multi-ester having a molecular weight of not more than 750.

In the present invention in describing cleaning media as "detergent free" we mean that they do not include amphiphilic materials that aid soil removal from textiles. In describing cleaning media as "micelle free" we mean that the cleaning medium does not contain micelles of cleaning additives.

We have found that the presence of detergents including those which may form micelles in liquid CO₂ can reduce the effectiveness of the cleaning additives used in the invention.

The cleaning additive multi-esters used in this invention are desirably of the formula(I):



5 where

X is -C(O)O- or -OC(O)- ; such that

where X is -C(O)O-,

R¹ is a direct bond or the residue of a C₁ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed; and

10 R² is a C₁ to C₁₀ hydrocarbyl group; and

where X is -OC(O)-,

R¹ is or the residue of a C₂ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed; and

R² is H or a C₁ to C₁₀ hydrocarbyl group; and

15 n is from 2 to 5;

the compound having a molecular weight of not more than 750.

These cleaning additive multi-esters can be divided into two sub-classes respectively of the formulae (Ia) and (Ib) below. Compounds of the formula (Ia) are esters of a multi-carboxylic acid and a mono-hydroxy alcohol:



where

X is -C(O)O-;

R^{1a} is a direct bond or the residue of a C₁ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed;

25 R^{2a} is a C₁ to C₁₀ hydrocarbyl group; and ;

the compound having a molecular weight of not more than 750.

Examples of compounds of the formula (Ia) include di-esters of dicarboxylic acids such as succinic, glutaric and adipic acids.

Compounds of the formula (Ib) are esters of a monocarboxylic acid and a multi-hydroxy alcohol:



where

X is -OC(O)- ;

R^{1b} is or the residue of a C₂ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed; and

35 R^{2b} is H or a C₁ to C₁₀ hydrocarbyl group; and

the compound having a molecular weight of not more than 750.

Examples of compounds of the formula (Ib) include esters of multi-hydroxyl compounds such as triacetin (glycerol triacetate), ethylene glycol diacetate and pentaerythritol tetra-acetate.

The precise mode of action of the multi-ester cleaning additives is not clear. They do appear to boost the overall cleaning performance of liquid CO₂ but operating at levels that are significantly lower than that would be expected to be effective if the effect were simply additive co-solvency. In addition the use of these additives gives improved handling of textiles cleaned using them as compared with no cleaning additives or commercially available detergents for use in liquid CO₂.

Within the formula (I) above, generally is desirable that the group X is -C(O)O- as these compounds seem to provide superior effects in cleaning. Among such compounds, the group R¹ is desirably -(CH₂)_m- where m = 2 to 6, particularly 2 to 4 and especially as in the mixed ester of succinic, glutaric and adipic acids; and the group R² is desirably methyl, ethyl or propyl, particularly methyl. Thus, the dimethyl esters of succinic, glutaric and adipic acids, particularly as mixtures are particularly desirable additives.

The molecular weight of the cleaning additive is not more than 750 and is desirably not more than 500. In practice the molecular weight for individual components e.g. of formula (I) can be as low as 118 (dimethyl oxalate) but will not usually be lower than 146 (dimethyl succinate and ethylene glycol diacetate). More usually on average the molecular weight will be at least 150, particularly from 150 to 300. The mixed dimethyl esters of succinic, glutaric and adipic acids can have molecular weights ranging from about 150 to 170 e.g. for an approximately 1:1:3 mixture the average molecular weight is about 165.

In order to maintain the desired high polarity, the ratio of oxygen to carbon atoms in the molecules of the cleaning additive is (on average) desirably from from 1:1 to 1:5 particularly from 1:1 to 1:3 and especially from 1:1 to 1:1.5. The mixed dimethyl esters mentioned above have an average ratio of ca 1:1.23.

The amount of cleaning additive multi-ester present in the cleaning medium is from 0.01 to 5%, usually from 0.05 to 2%, more usually from 0.1 to 1%, particularly from 0.1 to 0.5% and more particularly from 0.1 to 0.3% by weight of the cleaning medium. The use of lower amounts of cleaning additive will not generally give useful results and use of larger amounts does not appear to give additional benefits and may result in including so much additive in the system that additive residues are deposited onto the textiles being cleaned or left on the walls of the cleaning apparatus.

Other ingredients can be included in the dry cleaning formulation such as fragrances, optical brighteners, fabric conditioners such as softeners, and sizes e.g. starch, enzymes, bleaches, particularly peroxide bleaches e.g. organic and/or inorganic peroxides or hydrogen peroxide or a source of hydrogen peroxide.

The textiles to be cleaned will usually be garments and can be of woven or non-woven fabrics. The fibre making up the fabric can be or include a wide range of natural and synthetic fibres including polyamides particularly natural polyamides such as silk and wool and synthetic polyamides such as nylon, cellulosic fibres such as cotton, linen and rayon, synthetic polymers such as polyester, particularly polyethylene terephthalate or related copolymers, or acetate polymers. When fabrics including acetate polymers and possibly nylon polymers are cleaned it is best to avoid direct contact between the fabric and high concentrations of or neat multi-ester additives. When neat or at high concentration, the multi-ester additives may swell or dissolve such polymers leading to fabric damage. Thus it is desirable to pre-mix the multi-ester with CO₂ before permitting contact with such polymers. Pre-mixing the multi-ester cleaning additive with CO₂ to give a concentration of less than about 10%, more usually less than 5%, and desirably not more than 2% by weight of the cleaning additive in the liquid CO₂ based cleaning medium before the additive comes into contact with the textile seems to avoid this potential problem.

The particular mode of operation will depend on the equipment used. Generally the cleaning will be carried out in a drum, which may have its axis vertical or horizontal. The textiles are introduced into the drum which is then sealed and filled with the cleaning medium including carbon dioxide typically to give a mixture of liquid and gaseous CO₂ in the drum. The textiles and liquid CO₂ based cleaning medium are then agitated to give thorough mixing and contact between the cleaning medium and textiles. The textiles will be contacted with the cleaning medium for a time adequate to clean the textiles to the desired extent. The cleaning medium is then separated from the textiles, typically by draining or venting it from the drum. Generally the textiles will be subject to one such cleaning cycle, but if desired the cleaning cycle may be repeated to obtain a higher degree of cleaning. Usually, the textiles are subject to at least one rinse cycle with liquid carbon dioxide usually not including cleaning additives, but which may include fabric softeners, optical bleaches etc if desired. The rinse liquid is similarly separated from the textiles, which can then be recovered by de-pressurising the drum and opening it to remove the textiles.

Any suitable apparatus for dry cleaning with liquid carbon dioxide can be used. Typically such apparatus includes a drum in which the cleaning is carried out. The drum may have its axis horizontal or vertical. (Other angles of orientation will generally be less convenient in operation.) Providing agitation in a horizontal axis drum can simply be by rotation around its axis. Vertical axis drums will usually include an agitator which can be moved to agitate the drum contents. Other means of agitation include paddles or vanes in the drum or by jetting liquid CO₂ into the mixture of cleaning medium and textiles in the drum. Suitably vigorous agitation may give rise to cavitation in the cleaning medium and this may improve the cleaning performance.

Typically the cleaning temperature will be from -10 to 25°C, more usually from 5 to 25°C, particularly from 10 to 20°C. The operating temperature will not usually be above about 25°C to maintain the cleaning medium a reasonable margin from the critical point of CO₂, as supercritical

CO₂ may extract textile dyes from fabrics. Operating at or near ambient temperature simplifies operation of the process, but using a lower temperature means that the CO₂ is more dense and a more effective cleaning agent. Temperatures in the range 10 to 17°C, particularly 12 to 15°C generally provide a reasonable balance of properties and are thus advantageous.

- 5 During cleaning the cleaning medium must be kept at a pressure which maintains the CO₂ at least partially as a liquid. This will usually be the vapour pressure of the cleaning medium at the temperature of operation because, as is noted above, it is desirable for both liquid and gaseous CO₂ to be present. At the typical operating temperatures noted above, the corresponding pressures are approximately 2.7 to 6.4 MPa, more usually from 4 to 6.4 Mpa, particularly from 4.5 to 5.7 Mpa and balancing density and temperature 4.5 to 5.5 Mpa, particularly from 4.9 to 5.1 Mpa.
- 10

The invention is illustrated by the following Examples. All parts and percentages are by weight unless otherwise indicated.

Materials

- CA1 mixed esters: dimethyl adipate (ca 60%), dimethyl glutamate (ca 20%), and dimethyl succinate (ca 20%)
- CA1a additive CA1 plus a fragrance
- CA2 mixed esters: dimethyl adipate (ca 90%) and dimethyl glutamate (ca 10%)
- CA3 dimethyl adipate
- CA4 triacetin
- CD1 Kreussler - conventional formulated detergent
- CD2 Fabritech 5565 - conventional formulated detergent
- CD3 Conventional detergent (composition not known)

Cleaning testing used standard "Krefeld" stained cloths. The codes for these cloths include a number indicating the fabric type and a letter or letters indicating the soil as follows:

Cloth Type		Soil Type			
10	cotton	C	WFK soil*/lanolin mix	GM	used motor oil
20	polycotton	D	sebum	TE	clay
30	polyester (PET)	LS	Lipstick	PF	pigment/vegetable fat

- * WFK soil - a mixed soil based on kaolinite and containing soot and iron oxide pigments

Cleaning effectiveness - was assessed spectrometrically (using an X-Rite Spectrophotometric Colour Measurement system) by comparison of commercially available standard soiled cloths before and after cleaning with the results given as % stain removal.

Example 1

- Various cleaning additives were tested for efficacy in removing stains from standard stained cloths using the experimental cleaning machine and method set out below.

Test Cleaning Procedure

- An experimental cleaning machine is based on a pressure cylinder ca 50 cm long by 15 cm diameter (external); internal volume ca 6 l as the cleaning vessel. Connections are provided to enable the cylinder to be filled with carbon dioxide and emptied and for holding test cloths in the vessel.

- Soiled fabric samples are held in place inside the pressure cylinder, the desired additive is introduced into the bottom of the cylinder using a syringe and the cylinder sealed. The cylinder is filled initially with gaseous carbon dioxide (to a minimum of 30 bar pressure) and then the desired quantity, usually from 1.5 to 2.0 kg (measured by logging the weight loss of the supply cylinder), of liquid carbon dioxide is introduced. The supply connections are removed and the test cylinder is rotated end over end for a predetermined time. The cylinder

is then suspended with its axis vertical so that the 'dirty' liquid drains away from the washed fabric samples under gravity. The 'dirty' liquid CO₂ is vented to atmosphere. A rinse stage is normally carried out by repeating the filling process but without using any cleaning additive. The fabric samples are then removed from the machine removed and the stains examined using a computer controlled spectrophotometric colour measurement system.

The cleaning conditions and the results obtained are set out in Table 1 below

Table 1

Ex No	Wash Time (min)	Rinse Time (min)	Final Press. (Bar)	Temp (°C)	Additive		% Soil Removed				
					type	(%w/w)	30C	30D	10LS	10PF	10GM
1.C.1	15	0	50	16	none	-	25	35	27	23	24
1.C.2	15	15	50/51	13/15	CD1	0.2	28	39	29	29	26
1.1	15	15	50	15	CA1	0.2	36	41	38	28	28
1.2	15	15	45	12	CA1	0.2	33	32	30	23	24
1.3	15	15	48	14	CA2	0.2	20	34	29	19	19
1.4	15	15	-	-	CA3	0.2	33	42	30	25	27

Example 2

Further tests were carried out in commercial scale liquid CO₂ dry cleaning equipment using standard Krefeld soiled cloths, pinned to blank textile sheets to provide more realistic behaviour in the cleaning machine. The results are set out in Table 2 below:

Table 2

Ex No	Additive		30C	30D	20MU	10LS	10PF	10TE	10GM
	type	amount							
2.1.C.1	none	-	42	55	31	36	38	18	26
2.1.C.2	CD2	0.2	20	35	21	32	29	14	22
2.1	CA1a	0.2	48	67	39	39	47	24	28
2.2.C.1	none	-	38	64	32	38	41	18	26
2.2.C.2	CD3	0.2	45	63	33	36	40	22	23
2.2	CA1a	0.2	45	69	32	39	45	23	24

The textiles cleaned using additive CA1a had a significantly improved feel as compared with cloths cleaned with liquid CO₂ alone or using the commercial detergent additives.

Claims

1 A detergent free dry cleaning medium based on liquid CO₂ and including from 0.01 to 5% by weight of the cleaning medium of a cleaning additive which is at least one multi-ester having a molecular weight of not more than 750.

5 2 A dry cleaning formulation as claimed in claim 1 wherein the multi-ester includes at least one compound of the formula (I):



where

X is -C(O)O- or -OC(O)- ; such that

10 where X is -C(O)O-,

R¹ is a direct bond or the residue of a C₁ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed; and

R² is a C₁ to C₁₀ hydrocarbyl group; and

where X is -OC(O)-,

15 R¹ is or the residue of C₂ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed; and

R² is H or a C₁ to C₁₀ hydrocarbyl group; and

n is from 2 to 5;

the compound having a molecular weight of not more than 750.

20 3 A dry cleaning formulation as claimed in claim 2 wherein the multi-ester is of the formula (Ia):



where

X is -C(O)O-;

25 R^{1a} is a direct bond or the residue of a C₁ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed;

R^{2a} is a C₁ to C₁₀ hydrocarbyl group; and

4 A dry cleaning formulation as claimed in claim 3 wherein the multi-ester is a dimethyl ester of adipic, glutaric or succinic acids or a mixture of such esters.

5 A dry cleaning formulation as claimed in any one of claims 1 to 4 wherein the average
30 molecular weight of the multi-ester(s) is from 150 to 300.

6 A dry cleaning formulation as claimed in any one of claims 1 to 5 wherein the average ratio of oxygen atoms to carbon atoms in the multi-ester(s) is from 1:1 to 1:5.

7 A dry cleaning formulation as claimed in claim 6 wherein the average ratio of oxygen atoms to carbon atoms in the multi-ester(s) is from 1:1 to 1:1.5.

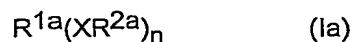
8 A dry cleaning formulation as claimed in any one of claims 1 to 7 wherein the amount of cleaning additive multi-ester present in the cleaning medium is from 0.1 to 0.5% by weight of the cleaning medium.

9 A dry cleaning formulation as claimed in any one of claims 1 to 8 which additionally includes at least one fragrance, optical brightener, fabric conditioner, enzyme and/or bleach.

10 A method of dry cleaning which includes contacting textile material with a detergent free dry cleaning medium based on liquid CO₂ and including from 0.01 to 5% by weight of the cleaning medium of a cleaning additive which is at least one multi-ester having a molecular weight of not more than 750.

11 A method as claimed in claim 10 wherein the multi-ester includes at least one compound of the formula (I): $R^1(XR^2)_n$ where X, R¹, R² and n are as defined in claim 2, the compound having a molecular weight of not more than 750.

12 A method as claimed in claim 11 wherein the multi-ester is of the formula (Ia):



where

X is -C(O)O-;

R^{1a} is a direct bond or a C₁ to C₁₀ hydrocarbyl group from which n hydrogen atoms have been removed;

R^{2a} is a C₁ to C₁₀ hydrocarbyl group; and

13 A method as claimed in any claim 12 wherein the multi-ester is a dimethyl ester of adipic, glutaric or succinic acids or a mixture of such esters.

14 A method as claimed in any one of claims 10 to 13 wherein the average molecular weight of the multi-ester(s) is from 150 to 300.

15 A method as claimed in any one of claims 10 to 14 wherein the average ratio of oxygen atoms to carbon atoms in the multi-ester(s) is from 1:1 to 1:1.5.

16 A method as claimed in any one of claims 10 to 15 wherein the amount of cleaning additive multi-ester present in the cleaning medium is from 0.1 to 0.5% by weight of the cleaning medium.

17 A method as claimed in any one of claims 10 to 16 which additionally includes at least one fragrance, optical brightener, fabric conditioner, enzyme and/or bleach.

18 A method as claimed in any one of claims 10 to 17 wherein the multi-ester is pre-mixed with liquid CO₂ before contacting the textiles.

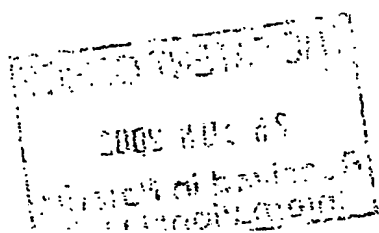
19 A method as claimed in any one of claims 10 to 18 wherein the cleaning process is carried out at a temperature of from -5 to 25°C.

- 20 A method as claimed in claim 19 wherein the temperature is from 5 to 20°C.
- 21 A method as claimed in claim 20 wherein the temperature is from 12 to 15°C.

Abstract

Cleaning Textiles

Detergent or micelle free cleaning media based on detergent free and/or micelle free liquid CO₂ and including from 0.01 to 5% by weight of the formulation of a cleaning additive which is at least one multi-ester having a molecular weight of not more than 750 can be used in dry cleaning of
 5 textiles. Desirable cleaning additives are of the formula (1): $R^1(XR^2)_n$ where X, R¹, R², and n have defined meanings, particularly to be esters of multi-carboxylic acids and mono-hydroxy alcohols or esters of mono-carboxylic acids and multi-hydroxy alcohols.



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